ful as catalyst supports, or they may be composed of other materials but coated with a suitable oxide carrier. Such structures may be conveniently treated by immersion in the noble-metal-ion-containing solution, and they may optionally be pretreated according to the aforementioned tin sensitization procedure by immersion in an acidified stannous chloride solution followed by immersion in water.

The process of the present invention is not limited to the treatment of large monolithic structures. The uniform deposition of a noble metal catalyst on a powdered oxide carrier is conveniently accomplished by simply dispersing the carrier in the selected treating solutions, and thereafter separating the treated carrier from the solution, for example, by filtration.

Aluminum oxide and tin oxide carriers are particularly suited for treatment according to the present invention because they promote the rapid deposition of the catalyst onto the carrier. For this reason, catalyst support structures comprising alumina, tin oxide, or coatings containing these carriers are preferred for treatment.
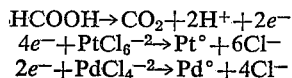
As sources of noble metal ions in the aqueous catalyst-containing solution, we prefer to employ soluble noble metal compounds which form halide-complexed noble metal ions such as $PtCl_6^{+2}$ and $PdCl_4^{-2}$ in aqueous solutions. Examples of preferred compounds include

$$H_2PtCl_6 \cdot 6H_2O,$$
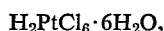
$PdCl_2 \cdot 2H_2O$, $RhCl_3 \cdot nH_2O$ and $AuCl_3$. However, in the case of silver, which forms an insoluble chloride, the nitrate is preferred. The noble metal ions may be present in the solution in essentially any desired concentration. However, low concentrations of noble metals, typically not exceeding about 5 milligrams of noble metal per milliliter of solution and desirably not exceeding an amount to be quantitatively deposited on an oxide carrier in a single application of the solution, are preferred for reasons of cost. Also, solutions containing platinum, palladium, rhodium and mixtures thereof are preferred for most catalyst applications.

Formic acid is used as the reductant in the process of the present invention because it is apparently unique in its capability of reducing the specified noble metal ions only in the immediate presence of an appropriate metal oxide carrier. Other known reducing agents either reduce and precipitate significant quantities of the noble metal present in the solution prior to the introduction of the carrier, or are ineffective to promote the desired degree of reduction and deposition even on the most active carriers such as alumina. The quantity of formic acid reductant present in the solution is not critical provided it is at least that stoichiometrically required to reduce the desired quantity of noble metal from the solution onto the carrier.

Preferably, the solution will contain only the amount of noble metal which is to be deposited in a single application, and complete or quantitative deposition of all of the noble metal from the solution will be desired. In that event, formic acid additions may range from about 1 to about 50 times the quantity stoichiometrically required to reduce all of the noble metal ions present in the solution to the metallic state. Representative oxidation-reduction reactions for the reduction of platinum and palladium by formic acid are shown below:

$$HCOOH \rightarrow CO_2 + 2H^+ + 2e^-$$
$$4e^- + PtCl_6^{-2} \rightarrow Pt^\circ + 6Cl^-$$
$$2e^- + PdCl_4^{-2} \rightarrow Pd^\circ + 4Cl^-$$

Concentrations of formic acid in excess of about 50 times the stoichiometric requirement should be avoided because they may cause some uncontrolled catalyst reduction, particularly at elevated temperatures.

The preparation of the aqueous solution containing noble metal ions and the formic acid reductant requires no special techniques or precautions. However, both the stability and the effectiveness of the solution are improved if

an at least slightly acidic condition is maintained therein. Solutions containing ammonum hydroxide as well as platinic and formic acid having pH values as high as about 9.4 have been prepared, but the deposition of noble metal from such solutions proceeds at a much slower rate. The pH values of typical acidic solutions normally range from about 1 to about 2 prior to use, and up to about 3.5 after deposition of the catalyst.

We have also found that the rate of noble metal deposition from solutions prepared as described can be increased by heating the solution and/or the oxide carrier during the contact interval. Thus the rate of deposition is considerably enhanced by carrying out the carrier-solution contact step at temperatures of 95° C. instead of at room temperature.

Following deposition of the metallic catalyst on the carrier, the carrier bearing the noble metal is typically dried at 110° C. and then further heated to remove residual water, formic acid, urea, etc. therefrom. The temperature and time of this treatment are not critical provided the heating is sufficient to remove these volatile residues. Heating at 500° C. for 1 hour in air, for example, is typically sufficient to treat ceramic honeycomb support structures.

The following specific examples illustrate in more detail the various techniques and procedures which are useful in carrying out the process of the present invention.

EXAMPLE I

A small ceramic monolithic support structure of the honeycomb type is provided. This structure is composed of a crystalline beta-spodumene solid solution, and is completely coated with a mixed-oxide coating consisting of about 80% alumina and 20% silica by weight. It is cylindrical in shape, about 1 inch in diameter and 2 5/16 inches in length, and comprises a multiplicity of parallel, axially-oriented, thin-walled channels or cells to be interiorly coated with a catalyst for the purpose of treating gases or fluids passing therethrough.

A solution consisting essentially of 10 ml. of a palladium chloride solution (containing 1.26 percent by weight of palladium), 25 ml. of distilled water, and 1 ml. of formic acid is prepared. The ceramic support structure described above is completely immersed in this solution, and the vessel containing the solution and structure is immersed in a 95° C. water bath.

After two minutes of heating in this water bath, the ceramic support structure becomes black in appearance, indicating the presence thereon of a finely-divided metallic palladium coating. After five minutes of heating, the palladium solution, which was initially brown, becomes colorless, indicating that essentially all of the palladium has precipitated therefrom. No metallic palladium is visible within the reaction vessel except that present on the monolithic support structure.

After ten minutes of heating, the palladium-coated structure is removed from solution, dried, heated in a hot air oven at 500° C. for one hour to volatilize any residues, and finally tested for catalytic activity by insertion in a flowing gas stream containing carbon monoxide and propylene. The structure is very active in converting the carbon monoxide and propylene present in the gas stream to carbon dioxide and water, and would therefore be quite useful, for example, in the treatment of automotive exhaust gases to remove carbon monoxide and unburned hydrocarbons therefrom.

EXAMPLE II

A small ceramic monolithic support structure coated with an alumina-silica coating, essentially identical to the structure treated in Example I above, is selected for treatment.

A solution consisting essentially of 4 ml. of a chloro-platinic acid solution (containing 2 weight percent platinum), 26 ml. of distilled water, 0.370 grams of urea and 0.25 ml. of formic acid is prepared. The ceramic support